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ANODIC DEPOSITION OF MANGANESE DIOXIDE

BY

PETER MARX
TRANSLATED BY O. C. RALSTON

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ANODIC DEPOSITION OF MANGANESE DIOXIDE[1]

By Peter Marx[2]
Translated by O. C. Ralston[3]

INTRODUCTION

By O. C. Ralston

Natural or artificial manganese dioxide of a grade pure enough to be satisfactory as depolarizer for dry cells has never been available in large supply simultaneously with being available in desired quality. The Second World War called for more of it than ever. A supply of natural material from the Gold Coast was ample for the war and was not completely exhausted.

Whereas the crystal form of the manganese oxide was not recognized as a matter of importance until the war came, it is now known that gamma MnO_2 is a desirable form and that pyrolusite, once thought acceptable, is not the best mineral.

The following paper is a translation of an internal company report filed at the Bitterfeld office of the I. G. Farbenindustrie A.G. by Dr. Peter Marx in 1933, just a year after G. W. Nichols had published in the Transactions of the American Electrochemical Society a study of making anodic manganese dioxide from solutions of manganous sulfate. The I. G. experiments were made to confirm the American work and were also extended to a larger scale. Only chemical purity was considered, and no mention is made of crystal form. The report adds to the knowledge submitted by Nichols but has not been previously available to the general public. Believing it of value to the United States industry, a translation has been made.

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[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from United States Bureau of Mines Inf. Circ. 7464."
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Preparation of Artificial Manganese Dioxide by Anodic Oxidation of Manganous Sulfate

By Peter Marx[4]

In the electrolysis of manganous sulfate solution with nonattackable anodes, the latter are coated with deposited MnO_2. First divalent manganese ion is oxidized to tetravalent manganese ion: $MnSO_4 + SO_4 + 2\ (+) = Mn(SO_4)_2$. The manganic sulfate then decomposes hydrolytically into manganese dioxide and sulfuric acid: $Mn(SO_4)_2 + 2H_2O = MnO_2 + 2H_2SO_4$. This deposit of MnO_2 has a structure adapted to use as a depolarizer in dry cells. G. W. Nichols[5] carried out tests for the Burgess Battery Co. which it was now thought worth checking.

Nichols made his manganous sulfate by leaching a rhodochrosite ore ($MnCO_3$) with sulfuric acid and then removed iron from the solution. Reviewing the leaching and electrolytic operation, the following information is pertinent:

The electrolyte should contain 100 grams per liter of $MnSO_4$ + 33.5 grams of H_2SO_4 (hereafter called Nichols solution). The current density should be 0.6 to 1.0 amp. per dm.^{2}, the temperature about 90° C. With an electrode spacing of 2.5 cm., the bath voltage is 2.5 volts. The solution should be exhausted down to only 50 grams per liter $MnSO_4$ + 67 grams of H_2SO_4.

The cell solution is then regenerated by leaching more rhodochrosite, so the sulfuric acid is used cyclically.

Nichols used graphite cathodes and hard lead anodes with at least 5 percent Sb. The MnO_2 formed on the anodes in a coherent layer, which could reach as much as 6 mm. thick and was stripped. With a current efficiency of 70 percent, the energy consumption was 2.16 kw.-hr. per kilogram of MnO_2.

These specifications formed the basis of the tests recorded in table 1 of this paper.

Laboratory Tests

The current yields were measured by use of a copper coulometer. The MnO_2 content of the precipitate was made on samples that were well-washed, dried at 100° C. and dissolved in sulfuric acid solution containing ferrous sulfate with back titration of excess by permangante. For estimation of the total Mn the product was dissolved in H_2SO_4-H_2O_2 solution and then titrated with permanganate by the Volhard method.

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[4] Rept. 391, July 27, 1933: FIAT microfilm reel BB-187, 1604-18. PB L 73557. Bibliog. vol. 6, No. 9, p. 755.

[5] Trans. Am. Electrochem. Soc., vol. 62, 1932, p. 939.

TABLE 1. - Anodic deposition of MnO_2

Temp., ° C.	Electrode Anode	Cathode	Anode area, dm.^{2}	Amp.	Current density, amp. dm.^{2}	Volts	Amp. eff., percent	Energy consumption, kw.-hr./kg.	MnO_2, percent	Total Mn as MnO_2, gm.	Test No.
90	Pt	Pt	0.72	0.5	0.7	2.0	58.5	2.12	92.0	92.0	1
60	do.	do.	2.0	2.0	1.0	3.1	45.0	4.25	88.8	91.1	2
40	do.	do.	2.0	2.0	1.0	3.4	41.3	5.07	85.7	90.8	3
60	do.	do.	2.4	4.8	2.0	3.2	34.3	5.59	90.2	93.6	4
60	do.	do.	2.4	1.2	.5	2.3	53.1	2.68	91.9	95.9	5
90	PbSb	Graphite	2.6	2.0	.8	2.7	95.0	1.75	84.5	85.4	6
80	Pt	Pb	50	46	.9	3.0	76.0	2.43	92.0	94.0	7
80	do.	do.	50	50	1.0	2.6	68.6	2.31	94.5	94.6	8
85	do.	do.	50	100	2.0	3.1	56.0	3.42	94.0	94.0	9
80	PbSb	do.	50	48	1.0	2.9	54.6	3.14	89.5	90.5	10
85	Pt	Gra	25	37.5	1.5	3.7	56.4	4.0	95.0	95.0	11
80	MnO_2 on graphite	do.	2.0	2.0	1.0	2.4	55ca		90.7	93.5	12

(a) Influence of Temperature

In a glass beaker 1 liter of Nichols solution was electrolyzed between platinum electrodes with about 1 amp. per dm.^{2}. With constant current density, increase of temperature causes increase in current efficiency and in the MnO_2 content of the product, while the energy consumption decreases.

TABLE 2

Temp., ° C.	Current efficiency, percent	Energy, kw.-hr./kg. MnO_2	MnO_2 in ppt., percent	Test No.
90	58.5	2.12	92.0	1
60	45.0	4.25	88.8	2
40	41.3	5.07	83.7	3

(b) Influence of Current Density

Same conditions as in above, Nichols solution was electrolyzed between platinum electrodes at 60° C. Increasing the current density at constant temperature causes decreasing current efficiency, increasing energy consumption, and irregular changes in MnO_2 content of the product.

TABLE 3

Current density, amp./dm.^{2}	Current efficienty, percent	Energy consumption, kw.-hr./kg. MnO_2	MnO_2 in ppt., percent	Test No.
2	34.3	5.59	90.2	4
1	45.0	4.25	88.6	2
0.5	53.1	2,68	91.9	5

(c) Influence of Anode Material

At constant temperature and current density, the use of platinum and of hard lead anodes was compared. Use of the hard lead caused increased current efficiency over use of platinum, but decreased energy consumption and manganese dioxide content of the anode product.

TABLE 4

Temperature, 90° C.; 0.7 amp./dm.^{2}

Anode	Current efficiency, percent	Energy consumption, kw.-hr./kg. MnO_2	MnO_2 in ppt., percent	Test No.
Hard lead	95	1.75	84.5	6
Platinum	58.5	2.12	92.12	1

(d) Form of Anode Product

For the form of the MnO_2 precipitate, the current density and the material used in the anode are of the greatest importance. In table 1 (tests 1 to 4) all run with platinum electrodes, gave MnO_2 anode deposits which could be easily stripped by flexing the metal plate anode. In test 5 (0.5 amp./dm.^{2}) the deposit (shown in a photograph) was made up of dense scales perpendicular to the electrode surface and easily broken off by their own weight as they grew so that many of them detached and sank to the bottom of the bath. In test 6 of table 1, the deposit made on a hard lead anode was fairly adherent and part of it would require mechanical methods of removal. A portion remained which would demand chemical methods of removal. In this case only 14 ampere-hours were used and the layer was quite thin. It was tested whether a thicker deposit might not strip more easily by mechanical methods. Test 6 was therefore run with 72 ampere-hours. Also at change of current, the partially exhausted solution was replaced with fresh solution. This change in solution made the primary deposit a "finished" one and the younger layer of metal stripped easily from the earlier one. In practice, it would be expected that a two-step deposition would give easily stripped second layers.

(e) Alternating-Current Electrolysis

According to Kameyama and IIda (Metallborse 1932, p. 1183) it is possible to obtain a dry cell MnO_2 if the $MnSO_4$ solution is decomposed at the higher temperatures by use of alternating current.

Nichols' solution was kept cooled to about 40° C. and platinum gauze electrodes with 2 cm.^{2} electrode surface used for alternating current at current density of 50 amp./dm.^{2}. Around 10 to 11 amperes passed through the solution at 20 to 25 volts. Colored streams of material sank from the electrodes to the bottom and accumulated as a highly dispersed, difficultly filterable precipitate. The energy consumption was unreasonably high in comparison to the use of direct current.

Tests on Larger Scale

In two cells of 70 liters capacity, a few tests (Nos. 7 to 11 of table 1) were made of 2 to 3 days' duration. Exhausted solution was replaced by fresh material. The cells consisted of rectangular conical vessels with a drain at the lowest point. They were lead-lined and further protected with Keratex. Individual electrodes had a working surface of 25 $dm.^2$. Three sheet-lead cathodes were used between 2 platinum or hard lead anodes hung in the shape of cooling coils. Electrode spacing was 5 cm. To give constant temperature and concentration, the solution was blown with compressed air and evaporation losses made up periodically with distilled water.

Tests 7 and 8 with platinum electrodes were parallel or duplicate tests. The current efficiencies varied nearly 10 percent. Nichols also observed such deviations that had no visible explanation. Current efficiencies were higher than test 1 carried out on small scale with identical conditions. It is thought that there was a difference in structure of electrode surface. This difference is important in the nature of the product separated. Whereas in the small apparatus the deposit was adherent, in the larger-scale apparatus the product was a good filtering slime found on the bottom of the cell. Only on the edges and corners of the electrodes were there thick, dense crusts.

The energy consumption was about 14 percent larger than in the small tests. The MnO_2 content of the products was practically identical.

Test 9 shows the anticipated lowering of current efficiency with increase in current density.

One test, No. 10, with a hard-lead anode, gave a very poor current efficiency and very high energy consumption in comparison to laboratory test 6, which was also made with a hard-lead anode. It is obvious that the current efficiency varies one direction in large- and small-scale tests and is opposite to the variation for platinum anodes.

With respect to the impurity of the product due to lead (see below) one test (No. 11) with platinum anodes and graphite cathodes was carried out.

Testing of the Products in Batteries

Dr. Lange tested the products of tests 7 and 11 and one product made similar to No. 1, by taking discharge curves on test batteries. Using pure $MgCl_2$ electrolyte the following times of discharge were measured:

TABLE 5

Test No.	Total discharge time	Pb in product, percent
1 (similar to)	6 hr., 37 min.	0
7	3 hr., 14 min.	.02
11	5 hr., 32 min.	.02

The reading for No. 1 is to be regarded as normal. Column 3 of table 5 shows the lead contents of the products. It shows that the lead content of 0.2 percent depresses the discharge time by at least 50 percent. One must therefore work with a lead-free product.

In contrast to this observation is a remark made in discussion of the Nichols' work,[6] in which under the above conditions lead was present only in the form of PbO_2 and did no harm, whereas trouble was apparent when lead was present as the sulfate.

Electrode Question

Beside lead and platinum, it was decided to test out a few other anode materials.

V 2 a

No deposition of MnO_2 took place on a stainless steel of V 2 a type. The solution turned first yellow and then blue-green. It is known that iron depresses the current efficiency.

Magnetite

After about 6 hours, the solution showed a trace of iron, and the current efficiency was only 10 percent.

Artificial Manganese Dioxide from Manganese Nitrate by Thermal Decomposition

According to a patent by Siemens & Halske A.G. (German Patent 221,130, Kl.12 h ov 16/4/'10) it is possible to make MnO_2 electrodes by mixing pulverized, thermally prepared MnO_2 with manganese nitrate in thin batches and decompose thermally. This is based on the fact that the thermally generated compound is a conductor. A few electrodes were made up after this manner. The mechanical strength of such electrodes is low, and their electrical resistance is 5 to 6 times as great as that of graphite. Such electrodes of potential value in zinc sulphate electrolysis have hence not yet gone into practice.

Electrolytic Manganese Dioxide

It was sought to avoid use of thermally generated MnO_2 and substitute electrolytic MnO_2 on a carrier as electrode. However it is difficult because the electrolytic MnO_2 is a nonconductor.

A graphite plate was soaked for a long time in Nichols' solution, then coated with a layer of MnO_2. On turning on the current, currents of slime descend from the cathode to the bottom, because the MnO_2 again dissolves to $MnSO_4$. After a short time, however, the MnO_2 begins to precipitate in the openings of the graphite plate and to cling to it very tightly. This is a proof that the electrolysis cannot deposit onto MnO_2 made by electrolysis but under it, directly on the graphite; that is, the electrolytic MnO_2 is a nonconductor. Simultaneously it was deduced that the electrolytic layer of MnO_2 must be porous and that anodic migration of material does take place though it is hard to believe from the fracture of the MnO_2 which shows a dense gleaming appearance.

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[6] Work cited in footnote 5, p. 402.

Graphite Impregnated Thermally with MnO_2

Since thermally prepared MnO_2 is conductive, Dr. Balz has proposed to coat a graphite plate thermally by repeated dipping in manganese nitrate solution or melt, in order to impregnate it. It was needed to test whether an electrolytic coating of dense MnO_2 would be a protective coating and prevent anodic corrosion of the carrier.

To test out such plates, they are connected as anode in single cells with closed gas spaces and pneumatic fans. As a measure for corrosion, the CO_2 analysis of the cell gas was taken. The CO_2 content of the gases was first measured after some hours use of unimpregnated graphite anode. The gases carried 4 percent CO_2. Then an impregnated plate was used, and the gas contained only 0.3 percent CO_2 but was still slightly attacked.

Manganese nitrate solution wet graphite poorly. To test the importance of wettability the following was tried:

The graphite was dipped first into alcohol-water (L:1) because alcohol wets it well. It was then heated as long as alcohol vapors came off. Then it was cooled in water and soaked in concentrated manganese nitrate solution overnight. Then it was thermally treated. This regime was repeated four times. On electrolysis the platy impregnated layer was completely loosened in five minutes. Obviously dilution of the manganese nitrate solution by the wetting water was unfavorable.

In one test for 12 hours (No. 12, table 1) the current efficiency on a thermally prepared impregnated graphite anode was about 55 percent. The MnO_2 clung so tightly to the electrode that knocking off of the layer from the graphite, particularly from the corners, brings about a condition that favors corrosion of the graphite.

In all the impregnated pieces tested so far, the dipped graphite is put into a furnace and heated from the outside. It should be noted that the first MnO_2 particles form largely on the surface of the solution or within the solution. The impregnated layer therefore has mainly secondary particles in it. A denser impregnated layer should come from formation of primary particles and this should be possible if heating can come from within. Two parallel arc-light carbons were connected with a platinum wire and dipped into manganese nitrate. They were slowly heated by electricity conducted through them. This was repeated 20 times and the impregnated product then tested as anode. Within 5 hours the layer was perforated and the carbon corroded.

Different Metals and Alloys

A proposal was made by Dr. Pokorny to test a number of metals and alloys as anodes for deposition of MnO_2.

(a) Molybdenum. - The metal dissolved anodically without polarization in a Nichols solution.

(b) Tungsten. - The electrode was quickly covered with a dirty green layer.

(c) Molybdenum-Nickel. - The solution became green within 30 minutes.

(d) Ferrosilicon with 75 percent Si. - After 2 hours, iron can be detected in solution by thiocyanate test. In 72 hours the current efficiency was down to 34 percent.

(e) Ferrosilicon with 50 percent Si. - The electrode fell to powder and some coarse pieces.

(f) Molybdenum-Silicon. - Prepared by surface diffusion in iron. After 3 hours the solution is brown, and no MnO_2 is deposited.

(g) Molybdenum-Silicon. - Prepared by sintering the pulverized alloy constituents. After 6 hours the solution was slightly colored. MnO_2 deposition took place only in isolated spots.

(h) Tungsten-Cobalt-Chromium (Stellite). - The solution discolored, and no deposition of MnO_2 took place.

Summary

(1) The specifications of Nichols were confirmed. By tests in a cell of 70 liters volume and with platinum anodes the following data were collected:

Temperature, 80° C.
Tension, 3 volts.
Current density, 0.5-1 amp./$dm.^2$.
Current efficiency, 65 to 70 percent.
Energy consumed, 2.4 kw.-hr./kg. MnO_2.
MnO_2 in product, 92 percent.
Total Mn as MnO_2 in the product, 94 percent.

The product made on platinum anode is suitable for dry cells.

(2) With a graphite anode, current efficiency is 55 percent, and corrosion of the anode cannot be avoided.

(3) With a hard-lead anode, the current efficiency is 55 percent, and in addition the product is so contaminated with Pb that the life of a dry cell is shortened.

(4) Ten different metals and alloys were tested for utility as anodes but found unusable.

(5) Thermal impregnation of graphite with MnO_2 has not yet been successful.